added to the silicon-contained organic compound and $N_2O$.

Disclosure of Invention

In the low-dielectric insulating film and the barrier insulating film, nitrogen introduced into the film due to the film forming gas containing the nitrogen causes the problem. In the following, the problem caused by the nitrogen will be explained in detail.

Upon forming the via hole or the wiring recess in the low-dielectric insulating film or the barrier insulating film formed by the dual-damascene method using the film forming gas containing the nitrogen, when the chemically amplified photoresist for KrF or ArF to expose a line width of 0.13 $\mu$m or less is employed, there is a problem such that patterns intended by the design cannot be formed. According to various investigations, the cause of this phenomenon is estimated such that the nitrogen in the low-dielectric insulating film or the barrier insulating film is discharged to occasion excessively the crosslinking reaction of the resist. In particular, if not only $N_2$, $NH_3$, etc. but also $N_2O$ is employed as constitutive gases of the film forming gas of the low-dielectric insulating film and the barrier insulating film, this phenomenon tends to occur.

It is an object of the present invention to provide a semiconductor device manufacturing method capable of containing no nitrogen in a formed film or suppressing a nitrogen content to such an extent that a crosslinking reaction of the resist is not affected, while maintaining functions of respective films with regard to a film formation of a low-dielectric insulating film or a barrier insulating film, and a semiconductor device manufactured by the method.

The invention ~~set forth in Claim 1~~ is related to a semiconductor device manufacturing method, and it is characterized in comprising the steps of generating a film forming gas by using any one of a silicon-contained organic compound having a siloxane bond and a silicon-contained organic compound having a $CH_3$ group and in addition $H_2O$, and adjusting

a flow rate ratio of $H_2O$ to the silicon-contained organic compound to 4 or more and a gas pressure to 1.5 Torr or more; applying a power to the film forming gas to generate a plasma thereof so as to react it, and thus forming a low-dielectric insulating film on a substrate; generating a process gas containing at least any one of He, Ar, $H_2$ or deuterium; generating a plasma by applying a power to the process gas; and bringing the low-dielectric insulating film into contact with the plasma of the process gas.

The invention ~~set forth in Claim 2~~ is related to the semiconductor device manufacturing method ~~according to claim 1~~, and it is characterized in that the power applied to the film forming gas is a power having a frequency of 1 MHz or more.

The invention ~~set forth in Claim 3~~ is related to the semiconductor device manufacturing method ~~according to any one of claims 1 and 2~~, and it is characterized in that the power applied to the process gas is a power having a frequency of below 1 MHz.

The invention ~~set forth in Claim 4~~ is related to the semiconductor device manufacturing method ~~according to any one of claims 1 and 2~~, and it is characterized in that the power applied to the process gas is a power having a frequency of 1 MHz or more.

The invention ~~set forth in Claim 5~~ is related to the semiconductor device manufacturing method ~~according to any one of claims 1 to 4~~, and it is characterized in that a pressure of the process gas is adjusted to 1.0 Torr or less.

The invention ~~set forth in Claim 6~~ is related to the semiconductor device manufacturing method ~~according to any one of claims 1 to 4~~, and it is characterized in that a pressure of the process gas is adjusted to 0.5 Torr or less.

The invention ~~set forth in Claim 7~~ is related to the semiconductor device manufacturing method ~~according to any one of claims 1 to 6~~, and it is characterized in that, in the step of bringing the low-dielectric insulating film into contact with the plasma of the process gas, a temperature of the

low-dielectric insulating film is raised up to 375 ℃ or more.

The invention ~~set forth in Claim 8~~ is related to the semiconductor device manufacturing method ~~according to any one of claims 1 to 7~~, and it is characterized in that the step of bringing the low-dielectric insulating film into contact with the plasma of the process gas is followed by the further step of removing a surface layer of the low-dielectric insulating film.

The invention ~~set forth in Claim 9~~ is related to the semiconductor device manufacturing method ~~according to claim 8~~, and it is characterized in that the step of removing the surface layer of the low-dielectric insulating film is followed without bringing the low-dielectric insulating film into contact with an atmosphere by the further subsequent step of increasing a temperature of the low-dielectric insulating film to 375 ℃ or more at an atmospheric pressure or a low pressure, and then bringing the low-dielectric insulating film into contact with a process gas having a $CH_3$ group.

The invention ~~set forth in Claim 10~~ is related to a semiconductor device manufacturing method, and it is characterized in comprising the steps of generating a film forming gas by using any one of a silicon-contained organic compound having a siloxane bond and a silicon-contained organic compound having a $CH_3$ group and in addition $H_2O$, and setting a flow rate ratio of $H_2O$ to the silicon-contained organic compound to 4 or more and a gas pressure to 1.5 Torr or more; applying a power to the film forming gas to generate a plasma thereof so as to react it, and thus forming a low-dielectric insulating film on a substrate; and annealing the low-dielectric insulating film in an atmosphere of a nitrogen gas or an inert gas at a temperature of 400 ℃ or more.

The invention ~~set forth in Claim 11~~ is related to the semiconductor device manufacturing method ~~according to claim 10~~, and it is characterized in that the power applied to the film forming gas is a power having a frequency of 1 MHz or more.

The invention ~~set forth in Claim 12~~ is related to the

semiconductor device manufacturing method ~~according to claim 10 or 11~~, and it is characterized in that the step of annealing the low-dielectric insulating film is followed by the further step of removing a surface layer of the low-dielectric insulating film.

The invention ~~set forth in Claim 13~~ is related to the semiconductor device manufacturing method ~~according to claim 12~~, and it is characterized in that the step of removing the surface layer of the low-dielectric insulating film is followed without bringing the low-dielectric insulating film into contact with an atmosphere by the further subsequent step of increasing a temperature of the low-dielectric insulating film to 375 ℃ or more at an atmospheric pressure or a low pressure, and then bringing the low-dielectric insulating film into contact with a process gas having a $CH_3$ group.

The invention ~~set forth in Claim 14~~ is related to the semiconductor device manufacturing method ~~according to any one of claims 9 and 13~~, and it is characterized in that the process gas having the $CH_3$ group is a methylsilane consisting of any one of monomethylsilane ($SiH_3(CH_3)$), dimethylsilane ($SiH_2(CH_3)_2$), trimethylsilane ($SiH(CH_3)_3$), or tetramethylsilane ($Si(CH_3)_4$), or an alkoxysilane consisting of any one of trimethylmethoxysilane ($Si(CH_3)_3(OCH_3)$), dimethyldimethoxysilane ($Si(CH_3)_2(OCH_3)_2$), or methyltrimethoxysilane (TMS: $Si(CH_3)(OCH_3)_3$).

The invention ~~set forth in Claim 15~~ is related to the semiconductor device manufacturing method ~~according to any one of claims 1 to 14~~, and it is characterized in that a pressure of the film forming gas is adjusted to 1.75 Torr or more.

The invention ~~set forth in Claim 16~~ is related to the semiconductor device manufacturing method ~~according to any one of claims 1 to 15~~, and it is characterized in that, in the step of forming the low-dielectric insulating film, a temperature of the substrate is raised up to 25 ℃ or more but 400 ℃ or less.

The invention ~~set forth in Claim 17~~ is related to a semiconductor device manufacturing method, and it is

characterized in comprising the steps of generating a film forming gas by using any one of a silicon-contained organic compound having a siloxane bond and a silicon-contained organic compound having a $CH_3$ group and in addition $H_2O$, and setting a flow rate ratio of $H_2O$ to the silicon-contained organic compound to 12 or more; increasing a temperature of a substrate up to 200 ℃ or more but 400 ℃ or less; and applying a power to the film forming gas to generate a plasma thereof so as to react it, and thus forming a barrier insulating film on the substrate whose temperature is raised.

The invention ~~set forth in Claim 18~~ is related to the semiconductor device manufacturing method ~~according to claim 17~~, and it is characterized in that, in the step of generating the film forming gas, a pressure of the film forming gas is adjusted to below 1.0 Torr and, in the step of forming the barrier insulating film, a power of a frequency of below 1 MHz is applied to the substrate to bias the substrate and to generate a plasma of the film forming gas by the power of the frequency of below 1 MHz so as to react the plasma, and thus the barrier insulating film is formed.

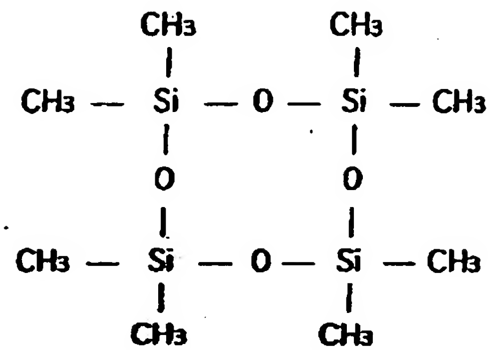
The invention ~~set forth in Claim 19~~ is related to the semiconductor device manufacturing method ~~according to claim 17~~, and it is characterized in that, in the step of generating the film forming gas, a pressure of the film forming gas is adjusted to below 1.0 Torr and, in the step of forming the barrier insulating film, a power of a frequency of below 1 MHz is applied to the substrate to bias the substrate while at least the power of the frequency of 1 MHz or more out of the power of the frequency of below 1 MHz or the power of the frequency of 1 MHz or more is applied to the film forming gas, whose pressure is adjusted to 1.0 Torr or more, to generate a plasma thereof so as to react it, and thus the barrier insulating film is formed.

The invention ~~set forth in Claim 20~~ is related to a semiconductor device manufacturing method, and it is characterized in comprising the steps of generating a film forming gas by using any one of a silicon-contained organic

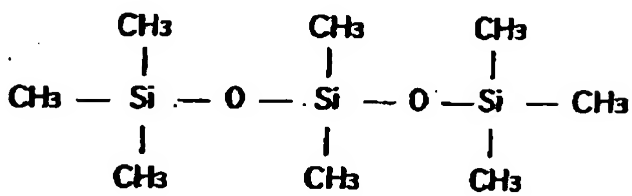
compound having a siloxane bond and a silicon-contained organic compound having a $CH_3$ group and in addition $H_2O$, and setting a flow rate ratio of $H_2O$ to the silicon-contained organic compound to 12 or more; adjusting a pressure of the film forming gas to below 1.0 Torr; increasing a temperature of a substrate up to 200 ℃ or more but 400 ℃ or less; applying the power of the frequency of below 1 MHz to the substrate to bias the substrate and to generate a plasma of the film forming gas by the power of a frequency of below 1 MHz so as to react the plasma, and thus forming a first insulating film; generating the film forming gas; adjusting a pressure of the film forming gas to 1.0 Torr or more; increasing a temperature of a substrate up to 200 ℃ or more but 400 ℃ or less; applying a power of a frequency of below 1 MHz to the substrate to bias the substrate while applying at least the power of the frequency of 1 MHz or more out of the power of the frequency of below 1 MHz or the power of the frequency of 1 MHz or more to the film forming gas, whose pressure is adjusted to 1.0 Torr or more, to generate a plasma thereof so as to react it, and thus forming a second insulating film on the first insulating film, whereby the barrier insulating film composed of the first insulating film and the second insulating film is formed.

The invention ~~set forth in Claim 21~~ is related to the semiconductor device manufacturing method ~~according to any one of claims 17 to 20~~, and it is characterized in that dinitrogen monoxide ($N_2O$) is added, or nitrogen ($N_2$) or ammonia ($NH_3$) is added, or dinitrogen monoxide ($N_2O$) and ammonia ($NH_3$) are added to the film forming gas.

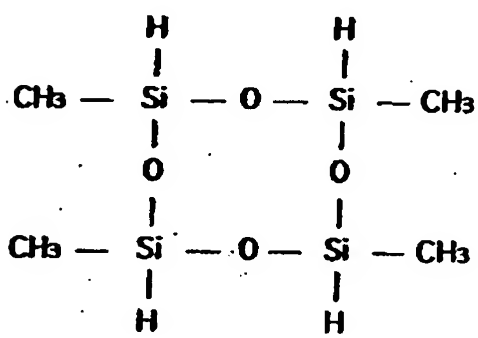
The invention ~~set forth in Claim 22~~ is related to the semiconductor device manufacturing method ~~according to any one of claims 1 to 21~~, and it is characterized in that the silicon-contained organic compound having the siloxane bond is any one of hexamethyldisiloxane (HMDSO: $(CH_3)_3Si-O-Si(CH_3)_3$), octamethylcyclotetrahexane (OMCTS)



octamethyltrisiloxane (OMTS), or

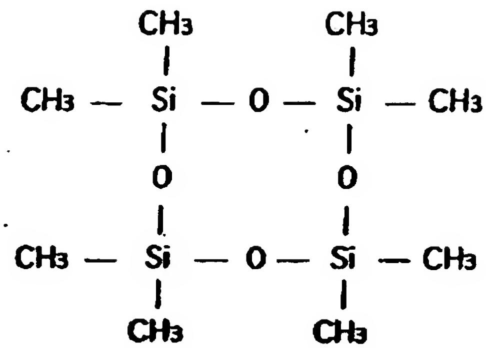


tetramethylcyclotetrasiloxane (TMCTS)

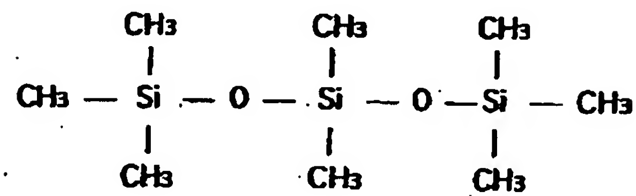


The invention ~~set forth in Claim 23~~ is related to the semiconductor device manufacturing method ~~according to any one of claims 1 to 21~~, and it is characterized in that the silicon-contained organic compound having the siloxane bond is a compound obtained by replacing at least one $CH_3$ group of any one of hexamethyldisiloxane (HMDSO: $(CH_3)_3Si\text{-}O\text{-}Si(CH_3)_3$),

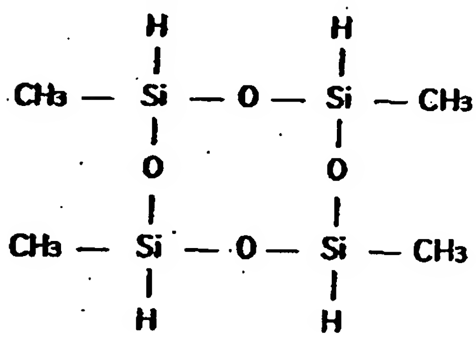
octamethylcyclotetrahexane (OMCTS)



octamethyltrisiloxane (OMTS), or



tetramethylcyclotetrasiloxane (TMCTS)



with F .

The invention ~~set forth in Claim 24~~ is related to the semiconductor device manufacturing method ~~according to any one of claims 1 to 23~~, and it is characterized in that the silicon-contained organic compound having the $CH_3$ group is a methylsilane consisting of any one of monomethylsilane ($SiH_3(CH_3)$), dimethylsilane ($SiH_2(CH_3)_2$), trimethylsilane ($SiH(CH_3)_3$), or tetramethylsilane ($Si(CH_3)_4$), or an alkoxysilane consisting of any one of trimethylmethoxysilane ($Si(CH_3)_3(OCH_3)$), dimethyldimethoxysilane ($Si(CH_3)_2(OCH_3)_2$), or

methyltrimethoxysilane (TMS: $Si(CH_3)(OCH_3)_3$).

The invention ~~set forth in Claim 25~~ is related to the semiconductor device manufacturing method ~~according to any one of claims 1 to 24~~, and it is characterized in that $C_xH_y$ (x, y are a positive integer), $C_xH_yF_z$ or $C_xH_yB_z$ (x, y are 0 (where, except the case x=y=0) or a positive integer, z is a positive integer) is added to the film forming gase.

The invention ~~set forth in Claim 26~~ is related to the semiconductor device manufacturing method ~~according to claim 25~~, and it is characterized in that $C_xH_y$ is $C_2H_4$.

The invention ~~set forth in Claim 27~~ is related to the semiconductor device manufacturing method ~~according to claim 25~~, and it is characterized in that $C_xH_yF_z$ is $C_3F_8$, $C_4F_8$ or $CHF_3$.

The invention ~~set forth in Claim 28~~ is related to the semiconductor device manufacturing method ~~according to claim 25~~, and it is characterized in that $C_xH_yB_z$ is $B_2H_6$.

The invention ~~set forth in Claim 29~~ is related to a semiconductor device manufacturing method, and it is characterized in comprising the steps of forming the low-dielectric insulating film ~~by the semiconductor device manufacturing method set forth in Claim 1~~; and forming the barrier insulating film ~~by the semiconductor device manufacturing method set forth in Claim 17 or 20~~.

The invention ~~set forth in Claim 30~~ is related to a semiconductor device manufacturing method, and it is characterized in comprising the steps of forming the low-dielectric insulating film ~~by the semiconductor device manufacturing method set forth in Claim 10~~; and forming the barrier insulating film ~~by the semiconductor device manufacturing method set forth in Claim 17 or 20~~.

The invention ~~set forth in Claim 31~~ is related to the semiconductor device manufacturing method ~~according to claim 29 or 30~~, and it is characterized in that the step of forming the low-dielectric insulating film is followed without exposing the low-dielectric insulating film to an atmosphere by the further subsequent step of forming the barrier insulating film.

The invention ~~set forth in Claim 32~~ is related to the semiconductor device manufacturing method ~~according to any one of claims 1 to 31~~, and it is characterized in that wirings or electrodes consisting mainly of a copper film are formed on the substrate.

The invention ~~set forth in Claim 33~~ is related to a semiconductor device ~~manufactured by the semiconductor device manufacturing method set forth in any one of claims 1 to 32~~.

Next, advantages achieved based on above configurations of the present invention will be explained hereunder.

According to the present invention, since $H_2O$ is used in place of $N_2O$ as the oxidizing gas, no nitrogen is contained in the formed film. The reason why other oxidizing gas such as $O_2$, or the like not containing the nitrogen is not used but $H_2O$ is used is that the film having the relatively good film quality can be formed. In particular, if the flow rate ratio of $H_2O$ to the silicon-contained organic compound is increased to 4 or more, for example, the film having the further good film quality can be formed.

Meanwhile, if the flow rate ratio of $H_2O$ to the silicon-contained organic compound is increased, the relative dielectric constant (k) tends to increase. In order to suppress such increase, upon forming the low-dielectric insulating film by the plasma CVD method, the plasmanizing frequency of the film forming gas is set high to 1 MHz or more and the gas pressure is set high to 1.5 Torr or more. Preferably, the gas pressure is set high to 1.75 Torr or more. In addition, for the same reason, the substrate temperature is set low to 400 ℃ or less during the film formation.

In this case, since many C-H, O-H, etc. whose bonding is considered as weak are contained in the formed film, the relative dielectric constant is still high such as 2.6 to 2.7 in contrast to the SOD film (Spin On Dielectrics). Therefore, C-H, O-H, etc. are discharged by applying the plasma process or the annealing process to the formed film after the film formation.